Non-methane Hydrocarbon (NMHC), Alkyl Nitrate, and Halocarbon Distributions from the NOAA WP-3D Aircraft during TexAQS II

E. Atlas, R. Lueb, X. Zhu, L. Pope (RSMAS, Univ. of Miami); S. Schauffler, R. Hendershot (NCAR, Atmos. Chem. Div.); R. Washenfelder, T. Ryerson, M. Trainer, K. Aikin, C. Brock, J. deGouw, C. Warneke, W. Kuster, P. Goldan (NOAA ESRL/CSD and CIRES); R. Peltier, R. Weber (GIT)

INTRODUCTION

During the recent Texas Air Quality Study [TEXAQS II (2006)] campaign, we measured a wide range of volatile organic compounds (VOC) from whole air samples collected during flights of the NOAA P3B (Table 1). Target compounds were selected to represent major emission types of industrial, mobile, and natural emissions, as well as photochemical products formed during VOC oxidation. Similar measurements were conducted during a previous campaign (TEXAQS I; summer 2000). This investigation and other studies in the Houston region have demonstrated that volatile organic compounds (VOC) emitted from industrial and other sources contribute significantly to ozone and aerosol formation in the regional atmosphere.

This presentation provides a broad overview of the data set collected during the mission. Selected examples of the geographic distribution of different VOC are shown here. We also compare the statistical distributions of VOC concentrations in the Houston region measured in the campaigns of 2000 and 2006. From the measured concentrations of the target VOC compounds and their reaction rate with the OH radical, we quantify the OH reactivity of the organic trace gases represented in the whole air samples.

Table 1. Trace gases measured in whole air samples during TEXAQS_2006.

Hydrocarbons

Alkanes	Alkenes	Alkynes	Aromatics
methane	ethene	ethyne	Benzene
ethane	propene	propyne	Toluene
propane	1_butene		Ethylbenzene
isobutane	t_2_butene		m_p_xylene
n_butane	c_2_butene		o_xylene
cyclopentane	1_3_butadiene		Styrene
isopentane	cyclopentene		Isopropylbenzene
n_pentane	1_pentene		n_Propylbenzene
n_hexane	t_2_pentene		2_Ethyltoluene
2_methyl_pentane	c_2_pentene		3_Ethyltoluene
3_methyl_pentane	3_methyl_1_butene		4_Ethyltoluene
2_2_dimethylbutane	2_methyl_2_butene		1_3_5_Trimethylbenzene
2_3_dimethylbutane	2_methyl_1_butene		1_2_4_Trimethylbenzene
cyclohexane	isoprene		1_2_3_Trimethylbenzene
n_heptane	a_Pinene		
2_methylhexane			
3_methylhexane			
n_octane			
2_2_4_Trimethylpentane			

Halocarbons

CFC_11	Methyl_chloride	Halon_1301
CFC_12	Ethyl_chloride	Halon_1211
CFC_113	Methyl_bromide	Halon_2402
CFC_114	n_Propylbromide	
CFC_115	Methyl_iodide	
HFC_134a	Dichloromethane	
HFC_152a	Vinyl_chloride	
HCFC_21	Chloroform	
HCFC_22	1_2_dichloroethane	
HCFC_123	Methyl_chloroform	
HCFC_124	Carbon_tetrachloride	
HCFC_141B	Trichloroethylene	
HCFC_142B	Tetrachloroethylene	
	Dibromomethane	
	Chlorodibromotmethane	
	Dibromoethane	
	Bromoform	

S,N,O VOC

S	N,O	O-VOC
Carbonyl_sulfide	Methyl_nitrate	Methyl_acetate
Dimethylsulfide	Ethyl_nitrate	Ethyl_acetate
	Isopropyl_nitrate	methacrolein
	n_Propylnitrate	methylvinyl_ketone
	2_butylnitrate	Methyl_t_butylether
	3_methyl_2_butylnitrate	2_butanone
	3_pentyl nitrate	furan
	2_pentyl nitrate	2_Methyl_Furan
		3_Methyl_Furan

SAMPLING AND ANALYTICAL

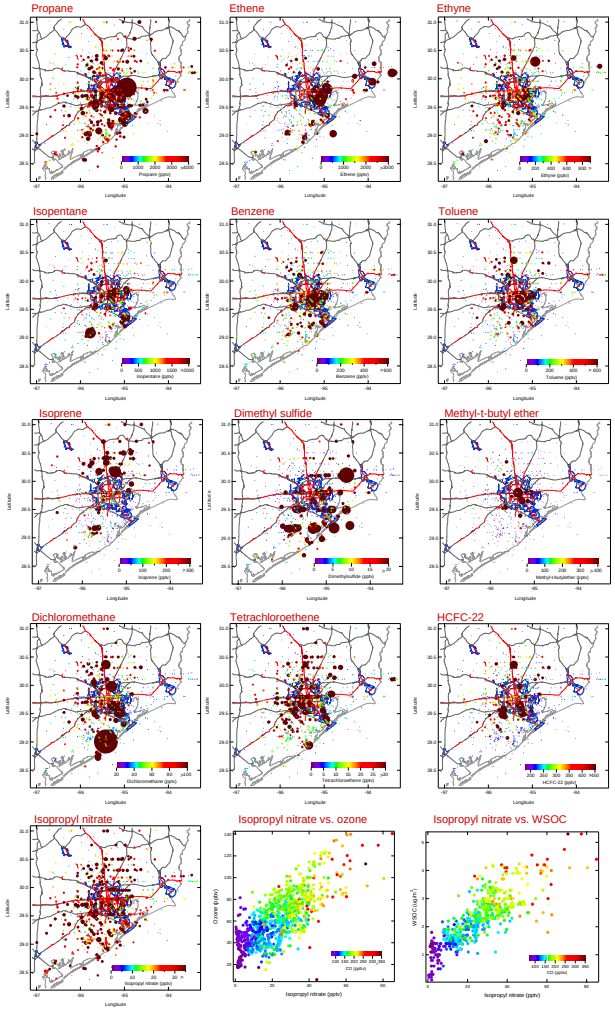
Figure 1. Whole Air Sampler (WAS) mounted in the right wing pod of the NOAA P3B for TexAQS 2006

The UM Whole Air Sampler was mounted in the right wing pod of the NOAA P3B aircraft. The sampler automatically, or on command, fills 80 stainless steel canisters (1.6 or 2.3 L) that have been precleaned and evacuated prior to flight. Typical fill times to a nominal pressure of 40 psia is approximately 10 seconds or less with a metal bellows compressor. Normal operation included a pre-programmed sample sequence with additional samples taken at the discretion of a scientist onboard to collect samples around specific plumes or at higher sample rates along expected gradients.

The samples were analyzed in the UM laboratory using the following instrumentation and techniques: 1) HP/Agilent 5971 and 5973 GC MS; 30m x 0.25 mm x 1μm non-polar (RTX-1) column, selected ion mode or SIM/SCAN mode (5973) for >C5 NMHC, halocarbons, organic nitrates, OVOC, etc.; 2) HP 5890 GC, 30 m Alumina (Na2SO4) column; FID for C2 – C5 NMHC; 3) HP 5890 GC, packed molecular sieve column: FID for methane. Standard gases were calibrated in-house using selected NIST primary standards, FID C response, and/or GC/Atomic Emission Detection, with comparison to other laboratories when possible.

GEOGRAPHICAL DISTRIBUTIONS

Distributions of selected trace gases are illustrated in the figures below. The data shown in the figures were selected to include samples collected at altitudes less than 2 km.



The distributions illustrated in the figures above reflect the different emission sources and patterns in the Houston region, and are similar to observations from TEXAQS 2000. Detailed analysis is yet to be done to identify all of the specific source emissions that are apparent in the hydrocarbon and halocarbon data.

In contrast to the very large concentration variation of primary hydrocarbon emissions, secondary products tend to be more uniformly distributed through the region. One example is shown for isopropyl nitrate, an oxidation product of propane. Correlation of isopropyl nitrate with other secondary gas and aerosol products (ozone and water soluble organic carbon in aerosol (WSOC)) is also shown.

ACKNOWLEDGMENTS. We thank D. Riemer (UM) for help with chromatographic analysis and standardization, C. Moore (UM) for technical assistance, and the crew and support team of the NOAA P3 aircraft for their contributions to the success of the TEXAQS mission. This work was supported by the NOAA Air Quality Program.

Statistical comparison of Houston region trace gas data: 2006 vs. 2000

Whole air samples collected during both the TEXAQS 2000 and 2006 campaigns targeted both background conditions as well as specific emission sources. At this point, we haven't yet analyzed the data set to determine the relative frequency of plume versus background sampling in the two campaigns. One comparison examines the basic statistics of the two data sets, and this is shown in Table 2. A comparison of the data is also possible with probability distributions, as shown in the figures below, which include selected WAS data as well as related trace gas measurements (CO, NOy, O3). From the WAS data, it appears that reactive alkenes are reduced in the top quartiles of the distribution (e.g. representative of emission sources), while median concentrations are similar in 2000 vs. 2006. In comparison, alkanes show higher median concentrations in 2006 vs. 2000, while near source concentrations (upper quartiles) were comparable or lower in 2006 vs. 2000. One peculiar feature that appeared in the analysis is for toluene. While other aromatic hydrocarbons tended to have probability distributions close to those of alkanes (e.g. higher medians, lower/comparable upper quartiles), toluene was uniformly elevated throughout the distribution in 2006 vs. 2000. The WAS data appears to be consistent with other airborne measurements taken during the two campaigns, but further examination with ground based data sets needs to be conducted to resolve this apparent anamoly.

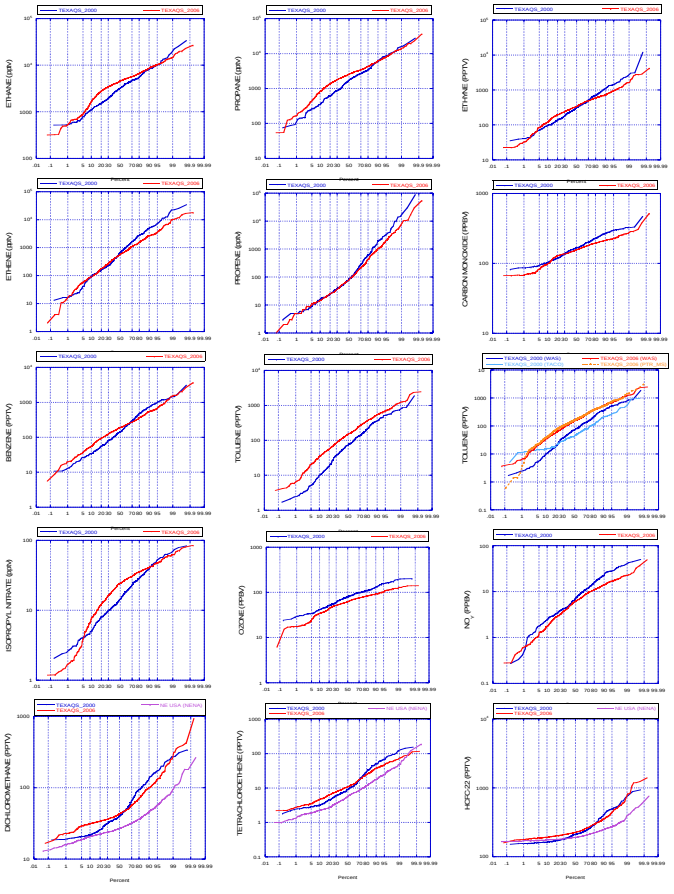


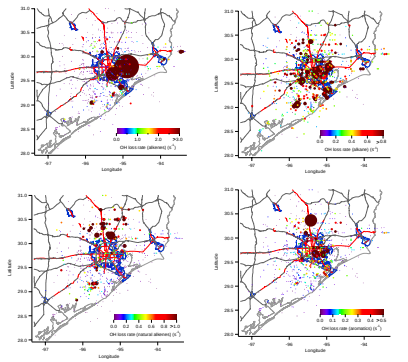
Table 2. Comparison of selected VOC measured from WAS and other parameters averaged over WAS sample times during TEXAQS 2000 and 2006 (<2km)

	TEXAQS 2006 (~790 pts)			TEXAQS 2000 (~300 pts)			RATIO (2006/2000)		
	Maximum	Mean	Median	Maximum	Mean	Median	Maximum	Mean	Median
methane	2277	1901	1904	2146	1818	1812	1.06	1.05	1.05
ethane	26870	4970	4598	33636	4138	3190	0.80	1.20	1.44
ethene	17890	1125	577	34617	1964	699	0.52	0.57	0.83
ethyne	4202	420	334	11957	510	318	0.35	0.82	1.05
propane	36523	3188	2569	27629	2627	1708	1.32	1.21	1.50
propene	54106	546	81	89034	1070	91	0.61	0.51	0.89
isobutane	15167	978	674	20947	1465	614	0.72	0.67	1.10
n_butane	12127	1344	985	7979	1049	611	1.52	1.28	1.61
1_3_butadiene	820	14	2	10922	65	1	0.08	0.22	1.29
isopentane	10003	744	487	9814	1028	431	1.02	0.72	1.13
n_pentane	3631	399	262	8512	545	240	0.43	0.73	1.09
isoprene	1437	93	41	3505	303	103	0.41	0.31	0.39
n_hexane	1498	165	109	1775	181	76	0.84	0.91	1.43
n_heptane	614	49	33	805	48	21	0.76	1.02	1.61
2_methylhexane	396	32	21	369	27	12	1.07	1.20	1.76
3_methylhexane	479	39	25	570	62	41	0.84	0.62	0.62
n_octane	243	21	13	1057	27	11	0.23	0.77	1.25
2_2_4_Trimethylpentane	19884	136	38	407	51	27	48.87	2.65	1.38
a_Pinene	79	5	2	34	5	3	2.32	1.03	0.67
Benzene	3668	263	192	3086	285	144	1.19	0.92	1.34
Toluene	2471	232	151	1879	140	73	1.32	1.66	2.08
Ethylbenzene	1044	44	25	581	40	16	1.80	1.11	1.51
m_p_xylene	1307	73	34	2975	78	20	0.44	0.93	1.72
o_xylene	435	28	15	660	29	10	0.66	0.96	1.56
HCFC_22	1393	261	226	935	248	210	1.49	1.05	1.08
HCFC_141B	64	22	21	84	18	18	0.76	1.20	1.19
HCFC_142B	42	21	21	25	16	16	1.67	1.30	1.28
Methyl_chloride	919	548	538	3005	559	533	0.31	0.98	1.01
Methyl_bromide	40	12	11	106	15	13	0.38	0.86	0.84
Dichloromethane	932	59	43	338	62	40	2.76	0.94	1.08
chloroform	200	18	17	512	18	12	0.39	1.02	1.44
methyl_chloroform	77	17	15	59	39	39	1.30	0.42	0.39
Tetrachloroethylene	117	17	11	154	19	9	0.76	0.86	1.19
Dibromomethane	2	1	1	4	1	1	0.50	0.99	1.03
Methyl_nitrate	13	5	4	11	4	4	1.17	1.16	1.27
Ethyl_nitrate	21	7	7	94	8	6	0.22	0.88	1.20
Isopropyl_nitrate	85	25	25	83	19	14	1.02	1.27	1.69
n_Propylnitrate	22	6	6	13	3	2	1.66	2.07	2.58
2_butylnitrate	128	33	30	108	21	14	1.19	1.57	2.21
3_methyl_2_butylnitrate	58	6	5	62	11	7	0.94	0.56	0.77
3_pentyl_nitrate	34	9	8	68	12	7	0.51	0.73	1.11
2_pentyl_nitrate	55	13	11	67	12	7	0.82	1.08	1.61
CO_ppbv_all	519	159	157	471	177	168	1.10	0.90	0.94
NOy_ppbv_all	49	7	6	50	10	7	0.99	0.71	0.86
NO_ppbv_all	7	1	0	18	1	0	0.38	0.61	0.70
NO2_ppbv_all	48	3	2	36	4	2	1.34	0.80	0.99
hno3_ppbv_all	10	2	2	14	4	3	0.69	0.66	0.74
O3_ppbv_all	141	64	61	202	84	80	0.70	0.76	0.77
SO2_ppbv_all	233	5	2	65	6	3	3.57	0.79	0.68
PAN_all	1925	530	453	1799	578	584	1.07	0.92	0.78
GpsAlt_all	2072	569	486	1955	629	637	1.06	0.91	0.76
GpsLat_all	31	30	30	31	30	30	1.01	1.00	1.00
GpsLon_all	-94	-95	-95	-94	-95	-95	0.99	1.00	1.00

Reactivity of VOC

The reactivity of VOC with OH is a measure of their contribution to oxidant production. Table 3 summarizes the reactivity of selected individual VOC (ranked by their median VOC reactivity) as well as of different compound groups. Whether ranked by median, mean or maximum OH reactivity (last not shown), light alkenes and C3 – C5 alkanes contribute most to the total VOC reactivity represented by the compounds reported from the WAS data. However, it should be noted that the VOC reported here will not represent the complete OH reactivity of VOC in Houston. Other compounds have been reported in the Houston atmosphere that are not included here at this time. Additional work is underway to examine the full mass spectral data collected for about 50% of the WAS samples in order to identify other VOC not originally targeted in the sample analyses.

The distribution of OH reactivity for different compound groups shown in Table 3 is illustrated in the figures below.

Table 3. OH reactivity (S^{-1}) of VOC measured from WAS during TEXAQS 2006. Top 25 VOC listed in order of decreasing median OH reactivity.

Variable	Mean	Median	Std. Dev.
OH_loss_rate_VOC	1.261	0.758	1.974
OH_loss_rate_alkane	0.400	0.311	0.393
OH_loss_rate_alkene	0.559	0.158	1.649
OH_loss_rate_nat_alkene	0.188	0.073	0.334
OH_loss_rate_aromatic	0.116	0.057	0.187
koh_CO_was	0.820	0.814	0.276
koh_no2_was	0.651	0.345	0.854
koh_methane	0.256	0.268	0.041
koh_ethene	0.189	0.083	0.331
koh_isoprene	0.183	0.071	0.328
koh_propane	0.077	0.063	0.073
koh_n_butane	0.071	0.053	0.078
koh_isopentane	0.059	0.039	0.076
koh_propene	0.286	0.037	1.442
koh_isobutane	0.046	0.031	0.056
koh_ethane	0.025	0.024	0.017
koh_n_pentane	0.033	0.022	0.038
koh_Toluene	0.028	0.016	0.034
koh_m_p_xylene	0.034	0.014	0.057
koh_n_hexane	0.019	0.013	0.021
koh_X2_methyl_pentan	0.015	0.011	0.017
koh_X1_butene	0.034	0.008	0.109
koh_X3_methyl_pentan	0.011	0.008	0.014
koh_cyclohexane	0.009	0.006	0.011
koh_ethyne	0.006	0.005	0.006
koh_n_heptane	0.007	0.005	0.008
koh_Styrene	0.020	0.005	0.090
koh_Benzene	0.007	0.005	0.008
koh_X2_methyl_1_butte	0.008	0.004	0.018
koh_o_xylene	0.008	0.004	0.011
koh_X3_methylhexane	0.005	0.004	0.006
koh_X3_Ethyltoluene	0.009	0.003	0.024
koh_Ethylbenzene	0.006	0.003	0.010